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Kinetics and mechanism of the Pudovik reaction in the azomethine series: III. Acid-catalyzed hydrophosphorylation of imines

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Abstract

A complex spectral (UV, IR, and 31P NMR), preparative, and kinetic investigation of the mechanism of the noncatalytic variant of the Pudovik reaction in the series of imines was carried out. The reaction proceeds through a four-center cyclic transition state. The transition state is highly labile, which determines its high sensitivity to the structure of the reagents, the nature of the solvent and catalyst, and some other factors. The necessary condition for the hydrophosphorylation of imines to occur is the participation of proton-donor reagents and acidic admixtures, specifically hydrolysis products of dialkyl hydrogen phosphites, such as monoalkyl dihydrogen phosphates and phosphorous acid, which act as acid catalysts. When the starting reagents are thoroughly purified and no such catalysts are present, the Pudovik reaction fails to occur in the imine series.

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